

(19) **SWISS CONFEDERATION**
FEDERAL OFFICE FOR INTELLECTUAL PROPERTY

(11)

CH 670 105 A5

(51)

Int. Cl.⁴:

C 23 C

18/12

C 01 B

21/064

C 04 B

41/50

Patent application issued for Switzerland and Liechtenstein
Treaty on patents dated December 22, 1978, between Switzerland and Liechtenstein

(12) **PATENT SECTION A5**

(21) Application number:3104/86	(73) Holder(s): Battelle Memorial Institute, Carouge GE
(22) Application date: 08/01/1986	
(24) Patent delivered on: 05/12/1989	(72) Inventor(s): Baumberger, Otto Bastian, Carouge GE
(45) Patent section published on: 05/12/1989	(74) Representative: Blasco Dousse, Carouge GE

(54) **Procedure for obtaining a corrosion-resistant boron nitride coating on a substrate**

(57) The object to be coated is immersed into a solution of solid borazine compounds, the solvent is then evaporated to leave a layer of said borazine compounds, then the object is pyrolysed, which converts said layer into a BN coating.

CLAIMS

1. Procedure to obtain on a substrate a homogeneous boron nitride coating, characterized by the fact that a layer of non-volatile or weakly volatile borazine derivative is applied onto a substrate and this substrate is then heated to pyrolyse the layer and convert it to BN with hydrogen evolution.
2. Procedure according to Claim 1, characterized by the fact that the substrate is heated at 600 - 800°C to obtain BN with a corrosion resistant amorphous structure.
3. Procedure according to Claim 2, characterized by the fact that the amorphous BN layer is then heated at 1100 - 1300°C, to convert it to hexagonal BN.
4. Procedure according to Claim 1, characterized by the fact that the borazine derivative is an oligomer of the latter, which is solid at an ambient temperature.
5. Procedure according to Claim 4, characterized by the fact that the oligomer is a dimer selected among the biborazinyll and the borazanaphthalene or a mixture of them.
6. Procedure according to Claim 1, characterized by the fact that, in order to perform the application, the substrate is immersed in a solution of the borazinic compound(s) so that a layer of this solution is formed on the surface of the substrate, then the solvent is evaporated from it in order to form a film of solid borazinic compounds on the surface of this substrate.
7. Procedure according to Claim 1, characterized by the fact that the solution of borazinic compound(s) is sprayed over the substrate maintained at a temperature high enough to cause the evaporation of the solvent and to form on the surface of the substrate a thin film of solid borazinic compounds.
8. Procedure according to Claim 6, characterized by the fact that for said solution is used an organic solvent selected among the high-aromatic solvents, such as benzene, toluene, xylene, etc., ethers such as tetrahydrofurane, dioxane, diglyme, and chlorinated solvents such as CHCl_3 , CH_2Cl_2 , trichloroethylene, etc.
9. Procedure according to Claim 8, characterized by the fact that the concentration by weight of the borazinic compounds in the solution is 1 to 50%.
10. Procedure according to Claim 2, characterized by the fact that over the substrate is directed, by sweeping according to a previously established pattern, an energetic or laser beam, a beam of electrons or ions, in order to produce on the affected area a local heating that converts the borazinic film into BN, and then to dissolve with a solvent the non transformed borazinic derivative, while the substrate keeps on the surface an area covered by boron nitride according to the original design.

DESCRIPTION

The subject of the present invention is a procedure to form, on a substrate, a boron nitride film resistant to corrosion by chemical and atmospheric agents. This non-conductive hard film, resistant to high temperatures in the air, acts as a protective coating for a large variety of substrates, preferably metal or mineral.

Numerous techniques to perform such a deposit are known from the state of the art.

It can be obtained by thermal decomposition of mixtures of BCl_3 and NH_3 (G. Male *et al.*, Laboratoires des Ultra-Réfractaires du CNRS, F. 66120 Font-Romeu, 1979) and of hexachloroborazine in vapor phase [G. Constant *et al.*, J. of the Less-Common Metals 82 (1981), pp. 113-118]. Diborane and ammonia can also be made to react in vapor phase (H.O Pierson *et al.*, Proceedings of the Seventh Internat. Conf. on CVD, The

Electrochemical Soc. Softbound Proceedings Series, Princeton, N.J. (1979), USA; US-A-4, 118, 211; as well as boron and nitrogen compounds such as trifluorotrimethylaminoborane and dibromodipropylamineborane [E.A. Balabanova *et al.*, Russian J. of Inorg. Chem. 25 (7), 1980, English translation, pp. 995-996.]. Decomposition of borazine was also performed in vapor stage [A.C. Adams, J. Electrochem. Soc., 128 (1981), pp.1378-1379] or in plasma stage [S. Shanfield *et al.*, G. Vac. Sci. Technol. A1 (2), April-June 1983, pp.323-324].

The BN films may be useful as dielectrics in microelectronics, as corrosion protection for chemical equipment, and as reinforcement and protection for glass or ceramic fibers used in telecommunications and composite materials.

The various above-mentioned preparation techniques show disadvantages connected to the instability of the starting materials and to the obligation to work in vapor phase under well controlled conditions that require the use of refractory reaction cells heated at a high temperature and of relatively complicated reactant vaporization equipment. Therefore, it was desirable to have a simplified procedure where a stable enough boron and nitrogen compound is allowed to react in order to be directly applied over the object to be coated, which is then simply heated at a temperature that is sufficient to cause the pyrolytic decomposition of said compound in a homogeneous layer that resists boron nitride corrosion.

Such a procedure is defined in Claim 1. Monomeric borazine is a liquid at ambient temperature and its vapor pressure is high. As a consequence, the liquid borazine film obtained on a substrate by immersion evaporates before the pyrolyse temperature is reached, even in autoclave; the product losses are too important to make this technique usable. On the contrary, by using a solid and little volatile derivative of borazine, for example an oligomer such as biborazinyl or borazanaphthalene, or mixtures of these substances, this disadvantage no longer exists.

In order to prepare such derivatives of borazine, it can be irradiated in vapor phase by means of an actinic source [M.A. Ness *et al.*, J.A.C.S. 94 (1972), p. 1438], which causes the formation of various oligomers besides the above mentioned dimers. Borazine can also be polymerized by heat (see A. Laubengayer *et al.*). All these substances can be used in the present invention, if they are soluble in volatile organic medium. Alkylated derivatives of these oligomers can also be used [see G.A. Kline *et al.*, Inorg. Chem. 16 (1977), p. 11].

In addition, the present inventor also found that the borazine oligomers can be prepared by exposure of liquid borazine, with the useful exposure in the visible and UV range. Traces of transition metals (Cr, Fe, Mo, W, etc.) can catalyze such a reaction.

For the implementation of the present invention, the following procedure is preferably used: a solution is prepared from the solid borazinic compound(s) in a neutral organic solvent, for example benzene, toluene, dioxane, THF, etc. and the coated object is immersed in this solution. This technique shows the considerable advantage of making all the elements on the surface of the object considered accessible for coating, even if they are hard to reach by gaseous reagents in case the usual coating techniques are applied. The object is then withdrawn from the solution and after draining, the solvent is allowed to evaporate, which leaves a thin film of the solid borazinic derivative on the surface of the object. There can be any concentration of borazinic derivative in the solution; the higher it is, the thicker the film obtained by evaporation. Practically, any concentration between 5 and 50% is suitable.

The object is then heated in a protective atmosphere furnace, for example with nitrogen or argon at sufficient temperature to cause the pyrolysis of the deposit and its conversion to BN with hydrogen evolution. This temperature is preferably between 600 and 800°C, which leads to a homogeneous amorphous deposit, resistant to corrosion by humidity and the usual corrosive chemical agents (HF, mineral and organic acids, alkaline hydroxides, NH₃, etc.).

Since the borazinic layer is very thin (on the order of a few μm to 500 μm), its pyrolytic decomposition is

very fast and only lasts between a few seconds and a few minutes (for example 10 sec. to 10 min.). Therefore, it is applicable both for a discontinuous and a continuous process during which the object (a tape, a filament or a series of objects arranged on a conveyor) is successively immersed in the solution, dried and heated by passage in a furnace at the selected temperature (everything being in inert atmosphere).

The amorphous deposit obtained at approximately 600 - 800°C can be crystallized by heating at a higher temperature: for example at approx. 1100 - 1300°C it is converted to hexagonal BN which, because of its structure, shows properties that are different from those of the amorphous layer, but which are also interesting from the industrial point of view.

Among the metal and mineral substrates that are suitable for the implementation of the present invention, one can mention articles with a surface made of a metal such as Ti, Mo, Fe, Mn, Cr, Co, Ni and other usual metals. On more noble metals, such as Cu, Ag, Au, Pt, Pd, etc., the application of the procedure is also possible, but the adherence is less satisfactory. As mineral substrates, one can mention Al_2O_3 , SiO_2 , ZrO_2 , glass, sandstone, ceramics, hard metals, metal borides, carbides and nitrides, etc.

The examples below illustrate the invention in detail.

Example 1:

In a standard quartz container were placed, under nitrogen protection, 100 g of liquid borazine that had been submitted to exposure to sunlight. After a few days, nitrogen distillation was performed, which supplied 26 g of non-distillable solid, the volatile portion being the borazine. This solid comprised a mixture of borazanaphthalene, biborazinyle and a low quantity of oligomers with higher molecular weight, whose structure was not determined.

Similar results were obtained by shorter exposure to a UV lamp that supplied a flow of 20 W/cm at a distance of 30 cm. In the presence of traces of transition metal compounds, the oligomerization time was shortened even more.

Example 2:

25 g of the solid obtained as described above were dissolved under nitrogen protection in 150 ml of dry benzene, and in this solution was immersed a bundle of approximately 20 g of alumina fibers with a diameter of 20 - 40 μm . This hank was removed from the solution and nitrogen-dried at 30 - 40°C until the solvent disappeared completely.

These fibers covered with a thin film of solid borazinic compounds were then rapidly heated at 800°C in nitrogen atmosphere, in an electric furnace. After a few minutes at this temperature, the hank was removed and the presence of a homogeneous film of amorphous boron nitride was observed on the fibers after SEM analysis. The thickness of this film was approximately 0.5 μm . By repeating this example with solutions of borazinic derivative having a concentration that varied between 2 and 35% per weight, similar films were obtained, with a thickness between 0.1 and 2 μm . Similar results were obtained on other substrates, for example fibers or wires made of SiO_2 , Fe, Ni.

By heating at 1250°C, the amorphous coating of part of these fibers was converted to adherent, insulating, non-porous hexagonal boron.

Example 3:

Under nitrogen protection, 25 g of borazinic solid were dissolved, as obtained per the description in Example 1, in 150 ml of dry toluene and in this solution was immersed continuously a silica optic fiber which was then dried under dry nitrogen at 60 - 80°C, until the solvent was completely eliminated. The surface of the fiber covered with a thin film of solid borazinic compounds was then rapidly heated at a

temperature between 600 and 800°C. A protective film of amorphous boron nitride and having a thickness on the order of 0.4 micron was obtained. This layer ensures protection against reagents, in particular against water, taking into consideration the hydrophile character of the layer. The layer also ensures a mechanical protection and gives the fiber a low coefficient of friction, which is very important for the manufacture of optic transmission cables.

Example 4:

Under nitrogen protection, 20 g of the solid were dissolved, as obtained per the description in Example 1, in trichloroethylene. This solution was gun-sprayed over the surface of a glass plate (a metal or ceramic surface could also be used) maintained at 80°C. After complete disappearance of the solvent, there remained on the surface a thin film of solid borazinic compounds. The substrate was then heated at temperatures between 600 and 800°C and a layer of amorphous silica nitride was thus obtained.

By heating at 1250°C, the amorphous coating was converted to adherent, insulating, non-porous hexagonal boron.

Example 5:

The same procedure as in Example 4 was followed, but instead of heating the entire substrate at a high temperature, a laser beam was directed over one portion of the latter, so that it only heated locally the fine film of solid borazinic compounds that covered it. A beam of electrons or ions can also be used. Thus was obtained, locally, a layer of adherent, insulating, non-porous hexagonal boron nitride. By immersing, under protective atmosphere, the substrate in the solvent used to dissolve the borazine oligomer, the layer of borazinic compounds that were not transformed in BN by the laser beam was eliminated. Using this technique, on the substrate was deposited a layer of adherent, insulating, non-porous hexagonal boron in the shape of an area of pre-established defined design. This technique can be also applied to metal, glass, ceramic and other substrates. As a consequence, this technique is of great interest in the field of electronic microcircuit manufacture.

(19) **SWISS CONFEDERATION**
FEDERAL OFFICE FOR INTELLECTUAL PROPERTY

(11)

CH 670 105 A5

(51)

Int. Cl.⁴:**C 23 C****18/12****C 01 B****21/064****C 04 B****41/50**

Patent application issued for Switzerland and Liechtenstein
Treaty on patents dated December 22, 1978, between Switzerland and Liechtenstein

(12) **PATENT SECTION A5**

(21) Application number: 3104/86	(73) Holder(s): Battelle Memorial Institute, Carouge GE
(22) Application date: 08/01/1986	
(24) Patent delivered on: 05/12/1989	(72) Inventor(s): Baumberger, Otto Bastian, Carouge GE
(45) Patent section published on: 05/12/1989	(74) Representative: Blasco Dousse, Carouge GE

(54) **Procedure for obtaining a corrosion-resistant boron nitride coating on a substrate**

(57) The object to be coated is immersed into a solution of solid borazine compounds, the solvent is then evaporated to leave a layer of said borazine compounds, then the object is pyrolysed, which converts said layer into a BN coating.

670 105

2

CLAIMS

1. Procedure to obtain on a substrate a homogeneous boron nitride coating, characterized by the fact that a layer of non-volatile or weakly volatile borazine derivative is applied onto a substrate and this substrate is then heated to pyrolyse the layer and convert it to BN with hydrogen evolution.
2. Procedure according to Claim 1, characterized by the fact that the substrate is heated at 600 - 800°C to obtain BN with a corrosion resistant amorphous structure.
3. Procedure according to Claim 2, characterized by the fact that the amorphous BN layer is then heated at 1100 - 1300°C, to convert it to hexagonal BN.
4. Procedure according to Claim 1, characterized by the fact that the borazine derivative is an oligomer of the latter, which is solid at an ambient temperature.
5. Procedure according to Claim 4, characterized by the fact that the oligomer is a dimer selected among the diborazinyll and the borazanaphthalene or a mixture of them.
6. Procedure according to Claim 1, characterized by the fact that, in order to perform the application, the substrate is immersed in a solution of the borazinic compound(s) so that a layer of this solution is formed on the surface of the substrate, then the solvent is evaporated from it in order to form a film of solid borazinic compounds on the surface of this substrate.
7. Procedure according to Claim 1, characterized by the fact that the solution of borazinic compound(s) is sprayed over the substrate maintained at a temperature high enough to cause the evaporation of the solvent and to form on the surface of the substrate a thin film of solid borazinic compounds.
8. Procedure according to Claim 6, characterized by the fact that for said solution is used an organic solvent selected among the high-aromatic solvents, such as benzene, toluene, xylene, etc., ethers such as tetrahydrofurane, dioxane, diglyme, and chlorinated solvents such as CHCl_3 , CH_2Cl_2 , trichloroethylene, etc.
9. Procedure according to Claim 8, characterized by the fact that the concentration by weight of the borazinic compounds in the solution is 1 to 50%.
10. Procedure according to Claim 2, characterized by the fact that over the substrate is directed, by sweeping according to a previously established pattern, an energetic or laser beam, a beam of electrons or ions, in order to produce on the affected area a local heating that converts the borazinic film into BN, and then to dissolve with a solvent the non transformed borazinic derivative, while the substrate keeps on the surface an area covered by boron nitride according to the original design.

DESCRIPTION

The subject of the present invention is a procedure to form, on a substrate, a boron nitride film resistant to corrosion by chemical and atmospheric agents. This non-conductive hard film, resistant to high temperatures in the air, acts as a protective coating for a large variety of substrates, preferably metal or mineral.

Numerous techniques to perform such a deposit are known from the state of the art.

It can be obtained by thermal decomposition of mixtures of BCl_3 and NH_3 (G. Male *et al.*, Laboratoires des Ultra-Réfractaires du CNRS, F. 66120 Font-Romeu, 1979) and of hexachloroborazine in vapor phase [G. Constant *et al.*, J. of the Less-Common Metals 82 (1981), pp. 113-118]. Diborane and ammonia can also be made to react in vapor phase (H.O Pierson *et al.*, Proceedings of the Seventh Internat. Conf. on CVD, The

Electrochemical Soc. Softbound Proceedings Series, Princeton, N.J. (1979), USA; US-A-4, 118, 211; as well as boron and nitrogen compounds such as trifluorotrimethylaminoborane and dibromodipropylamineborane [E.A. Balabanova *et al.*, Russian J. of Inorg. Chem. 25 (7), 1980, English translation, pp. 995-996.]. Decomposition of borazine was also performed in vapor stage [A.C. Adams, J. Electrochem. Soc., 128 (1981), pp.1378-1379] or in plasma stage [S. Shanfield *et al.*, G. Vac. Sci. Technol. A1 (2), April-June 1983, pp.323-324].

The BN films may be useful as dielectrics in microelectronics, as corrosion protection for chemical equipment, and as reinforcement and protection for glass or ceramic fibers used in telecommunications and composite materials.

The various above-mentioned preparation techniques show disadvantages connected to the instability of the starting materials and to the obligation to work in vapor phase under well controlled conditions that require the use of refractory reaction cells heated at a high temperature and of relatively complicated reactant vaporization equipment. Therefore, it was desirable to have a simplified procedure where a stable enough boron and nitrogen compound is allowed to react in order to be directly applied over the object to be coated, which is then simply heated at a temperature that is sufficient to cause the pyrolytic decomposition of said compound in a homogeneous layer that resists boron nitride corrosion.

Such a procedure is defined in Claim 1. Monomeric borazine is a liquid at ambient temperature and its vapor pressure is high. As a consequence, the liquid borazine film obtained on a substrate by immersion evaporates before the pyrolyse temperature is reached, even in autoclave; the product losses are too important to make this technique usable. On the contrary, by using a solid and little volatile derivative of borazine, for example an oligomer such as biborazinyl or borazanaphthalene, or mixtures of these substances, this disadvantage no longer exists.

In order to prepare such derivatives of borazine, it can be irradiated in vapor phase by means of an actinic source [M.A. Ness *et al.*, J.A.C.S. 94 (1972), p. 1438], which causes the formation of various oligomers besides the above mentioned dimers. Borazine can also be polymerized by heat (see A. Laubengayer *et al.*). All these substances can be used in the present invention, if they are soluble in volatile organic medium. Alkylated derivatives of these oligomers can also be used [see G.A. Kline *et al.*, Inorg. Chem. 16 (1977), p. 11].

In addition, the present inventor also found that the borazine oligomers can be prepared by exposure of liquid borazine, with the useful exposure in the visible and UV range. Traces of transition metals (Cr, Fe, Mo, W, etc.) can catalyze such a reaction.

For the implementation of the present invention, the following procedure is preferably used: a solution is prepared from the solid borazinic compound(s) in a neutral organic solvent, for example benzene, toluene, dioxane, THF, etc. and the coated object is immersed in this solution. This technique shows the considerable advantage of making all the elements on the surface of the object considered accessible for coating, even if they are hard to reach by gaseous reagents in case the usual coating techniques are applied. The object is then withdrawn from the solution and after draining, the solvent is allowed to evaporate, which leaves a thin film of the solid borazinic derivative on the surface of the object. There can be any concentration of borazinic derivative in the solution; the higher it is, the thicker the film obtained by evaporation. Practically, any concentration between 5 and 50% is suitable.

The object is then heated in a protective atmosphere furnace, for example with nitrogen or argon at sufficient temperature to cause the pyrolysis of the deposit and its conversion to BN with hydrogen evolution. This temperature is preferably between 600 and 800°C, which leads to a homogeneous amorphous deposit, resistant to corrosion by humidity and the usual corrosive chemical agents (HF, mineral and organic acids, alkaline hydroxides, NH₃, etc.).

Since the borazinic layer is very thin (on the order of a few μm to 500 μm), its pyrolytic decomposition is

670 105

4

very fast and only lasts between a few seconds and a few minutes (for example 10 sec. to 10 min.). Therefore, it is applicable both for a discontinuous and a continuous process during which the object (a tape, a filament or a series of objects arranged on a conveyor) is successively immersed in the solution, dried and heated by passage in a furnace at the selected temperature (everything being in inert atmosphere).

The amorphous deposit obtained at approximately 600 - 800°C can be crystallized by heating at a higher temperature: for example at approx. 1100 - 1300°C it is converted to hexagonal BN which, because of its structure, shows properties that are different from those of the amorphous layer, but which are also interesting from the industrial point of view.

Among the metal and mineral substrates that are suitable for the implementation of the present invention, one can mention articles with a surface made of a metal such as Ti, Mo, Fe, Mn, Cr, Co, Ni and other usual metals. On more noble metals, such as Cu, Ag, Au, Pt, Pd, etc., the application of the procedure is also possible, but the adherence is less satisfactory. As mineral substrates, one can mention Al_2O_3 , SiO_2 , ZrO_2 , glass, sandstone, ceramics, hard metals, metal borides, carbides and nitrides, etc.

The examples below illustrate the invention in detail.

Example 1:

In a standard quartz container were placed, under nitrogen protection, 100 g of liquid borazine that had been submitted to exposure to sunlight. After a few days, nitrogen distillation was performed, which supplied 26 g of non-distillable solid, the volatile portion being the borazine. This solid comprised a mixture of borazanaphthalene, biborazinyne and a low quantity of oligomers with higher molecular weight, whose structure was not determined.

Similar results were obtained by shorter exposure to a UV lamp that supplied a flow of 20 W/cm at a distance of 30 cm. In the presence of traces of transition metal compounds, the oligomerization time was shortened even more.

Example 2:

25 g of the solid obtained as described above were dissolved under nitrogen protection in 150 ml of dry benzene, and in this solution was immersed a bundle of approximately 20 g of alumina fibers with a diameter of 20 - 40 μm . This hank was removed from the solution and nitrogen-dried at 30 - 40°C until the solvent disappeared completely.

These fibers covered with a thin film of solid borazinic compounds were then rapidly heated at 800°C in nitrogen atmosphere, in an electric furnace. After a few minutes at this temperature, the hank was removed and the presence of a homogeneous film of amorphous boron nitride was observed on the fibers after SEM analysis. The thickness of this film was approximately 0.5 μm . By repeating this example with solutions of borazinic derivative having a concentration that varied between 2 and 35% per weight, similar films were obtained, with a thickness between 0.1 and 2 μm . Similar results were obtained on other substrates, for example fibers or wires made of SiO_2 , Fe, Ni.

By heating at 1250°C, the amorphous coating of part of these fibers was converted to adherent, insulating, non-porous hexagonal boron.

Example 3:

Under nitrogen protection, 25 g of borazinic solid were dissolved, as obtained per the description in Example 1, in 150 ml of dry toluene and in this solution was immersed continuously a silica optic fiber which was then dried under dry nitrogen at 60 - 80°C, until the solvent was completely eliminated. The surface of the fiber covered with a thin film of solid borazinic compounds was then rapidly heated at a

temperature between 600 and 800°C. A protective film of amorphous boron nitride and having a thickness on the order of 0.4 micron was obtained. This layer ensures protection against reagents, in particular against water, taking into consideration the hydrophile character of the layer. The layer also ensures a mechanical protection and gives the fiber a low coefficient of friction, which is very important for the manufacture of optic transmission cables.

Example 4:

Under nitrogen protection, 20 g of the solid were dissolved, as obtained per the description in Example 1, in trichloroethylene. This solution was gun-sprayed over the surface of a glass plate (a metal or ceramic surface could also be used) maintained at 80°C. After complete disappearance of the solvent, there remained on the surface a thin film of solid borazinic compounds. The substrate was then heated at temperatures between 600 and 800°C and a layer of amorphous silica nitride was thus obtained.

By heating at 1250°C, the amorphous coating was converted to adherent, insulating, non-porous hexagonal boron.

Example 5:

The same procedure as in Example 4 was followed, but instead of heating the entire substrate at a high temperature, a laser beam was directed over one portion of the latter, so that it only heated locally the fine film of solid borazinic compounds that covered it. A beam of electrons or ions can also be used. Thus was obtained, locally, a layer of adherent, insulating, non-porous hexagonal boron nitride. By immersing, under protective atmosphere, the substrate in the solvent used to dissolve the borazine oligomer, the layer of borazinic compounds that were not transformed in BN by the laser beam was eliminated. Using this technique, on the substrate was deposited a layer of adherent, insulating, non-porous hexagonal boron in the shape of an area of pre-established defined design. This technique can be also applied to metal, glass, ceramic and other substrates. As a consequence, this technique is of great interest in the field of electronic microcircuit manufacture.

①



CONFÉDÉRATION SUISSE
OFFICE FÉDÉRAL DE LA PROPRIÉTÉ INTELLECTUELLE

⑪

CH 670 105 A5

⑤

Int. Cl. 4: C 23 C 18/12
C 01 B 21/064
C 04 B 41/50

Brevet d'invention délivré pour la Suisse et le Liechtenstein
Traité sur les brevets, du 22 décembre 1978, entre la Suisse et le Liechtenstein

⑫ FASCICULE DU BREVET A5

⑳ Numéro de la demande: 3104/86

㉔ Date de dépôt: 01.08.1986

㉔ Brevet délivré le: 12.05.1989

㉔ Fascicule du brevet
publié le: 12.05.1989㉔ Titulaire(s):
Battelle Memorial Institute, Carouge GE㉔ Inventeur(s):
Baumberger, Otto Bastian, Carouge GE㉔ Mandataire:
Blasco Dousse, Carouge GE

㉔ Procédé pour obtenir un revêtement de nitrure de bore résistant à la corrosion sur un substrat.

㉔ On trempe l'objet à revêtir dans une solution de composés boraziniques solides, on évapore le solvant de manière à laisser subsister une pellicule desdits composés boraziniques, puis on soumet l'objet à la pyrolyse ce qui a pour effet de convertir ladite pellicule en un revêtement de BN.

REVENDICATIONS

1. Procédé pour obtenir sur un substrat un revêtement de nitrure de bore homogène, caractérisé par le fait qu'on applique sur ce substrat une couche d'un dérivé non volatil ou faiblement volatil de la borazine, puis qu'on chauffe ce substrat de manière à pyrolyser ladite couche et à la transformer en BN avec départ d'hydrogène.
2. Procédé suivant la revendication 1, caractérisé par le fait qu'on chauffe le substrat entre 600 et 800° C, le BN obtenu ayant une structure amorphe résistante à la corrosion.
3. Procédé suivant la revendication 2, caractérisé par le fait qu'ensuite on chauffe la couche de BN amorphe à 1100-1300° C, de manière à la convertir en BN hexagonal.
4. Procédé suivant la revendication 1, caractérisé par le fait que le dérivé de la borazine est un oligomère de celle-ci, solide à la température ambiante.
5. Procédé suivant la revendication 4, caractérisé par le fait que l'oligomère est un dimère choisi parmi le biborazinyne et le borazanaphtalène ou un mélange de ceux-ci.
6. Procédé suivant la revendication 1, caractérisé par le fait que, pour effectuer l'application, on trempe le substrat dans une solution du ou des composés boraziniques de manière que se forme à la surface de ce substrat une couche de cette solution, puis on évapore le solvant de celle-ci de manière à laisser un film de composés boraziniques solides sur la surface de ce substrat.
7. Procédé suivant la revendication 1, caractérisé par le fait qu'on pulvérise la solution du ou des composés boraziniques sur le substrat maintenu à une température suffisante pour provoquer l'évaporation du solvant et former à la surface du substrat un film mince de composés boraziniques solides.
8. Procédé suivant la revendication 6, caractérisé par le fait qu'on utilise, pour ladite solution, un solvant organique choisi parmi les solvants aromatiques tels que benzène, toluène, xylène, etc., des éthers tels que tétrahydrofuranne, dioxanne, diglyme, et des solvants chlorés tels que CHCl_3 , CH_2Cl_2 , trichloréthylène, etc.
9. Procédé suivant la revendication 8, caractérisé par le fait que la concentration pondérale de la solution en composés boraziniques est de 1 à 50%.
10. Procédé suivant la revendication 2, caractérisé par le fait qu'on dirige sur le substrat, et cela par balayage suivant un dessin préalable, un faisceau énergétique, laser, électrons ou ions, de manière à produire, sur la zone atteinte, un échauffement local transformant le film borazinique en BN, puis on dissout, par un solvant, le dérivé borazinique non transformé, le substrat conservant alors à sa surface une zone recouverte de nitrure de bore conforme au dessin original.

DESCRIPTION

La présente invention a pour objet un procédé pour former, sur un substrat, un film de nitrure de bore résistant à la corrosion par les agents chimiques et atmosphériques. Ce film, non conducteur, dur, résistant aux hautes températures à l'air, agit comme revêtement protecteur d'une grande variété de substrats, de préférence métalliques ou minéraux.

De nombreuses techniques pour effectuer un tel dépôt sont connues de par l'état de la technique.

Ainsi, on peut procéder par décomposition thermique de mélanges de BCl_3 et NH_3 (G. Male *et al.*, Laboratoire des Ultra-Réfractaires du CNRS, F. 66120 Font-Romeu, 1979) et de l'hexachloroborazine en phase vapeur (G. Constant *et al.*, J. of the Less-Common Metals 82 (1981), 113-118). On peut aussi faire réagir en phase vapeur le diborane et l'ammoniac (H.O. Pierson *et al.*, Proceedings of the Seventh Internat. Conf. on CVD, The Electrochemical Soc. Softbound Proceedings Series, Princeton, N.J. (1979), USA; US-A-4,118,211; ainsi que des composés de bore et d'azote tels que trifluorotriméthylaminoborane et dibromodipropylamineborane [E.A. Ba-

labanova *et al.*, Russian J. of Inorg. Chem. 25 (7), 1980, English translation, 995-996]. On a également procédé par décomposition de la borazine, sous forme de vapeur [A.C. Adams, J. Electrochem. Soc. 128 (1981), 1378-1379] ou de plasma [S. Shanfield *et al.*, G. Vac. Sci. Technol. A1 (2), April-June 1983, 323-324].

Les films de BN sont utiles comme diélectriques en microélectronique, comme protecteurs contre la corrosion dans des dispositifs de l'industrie chimique, ainsi que comme renforceurs et protecteurs de fibres de verre ou de céramiques dans les télécommunications et matériaux composites.

Les différentes techniques d'obtention évoquées ci-dessus présentent des inconvénients liés à l'instabilité des produits de départ ainsi qu'à l'obligation d'opérer en phase vapeur dans des conditions bien contrôlées qui exigent l'utilisation de cellules de réactions réfractaires chauffées à température élevée ainsi que de dispositifs de vaporisation des réactifs relativement compliqués. Il était donc désirable de disposer d'un procédé simplifié dans lequel on fait intervenir un composé de bore et d'azote suffisamment stable pour pouvoir être appliqué directement sur l'objet à revêtir, celui-ci étant ensuite simplement chauffé à une température suffisante pour provoquer la décomposition pyrolytique dudit composé en une couche homogène et résistante à la corrosion de nitrure de bore.

Un tel procédé est défini à la revendication 1. La borazine monomère est un liquide à température ambiante et sa pression de vapeur est élevée. En conséquence, un film de borazine liquide obtenu sur un substrat par trempage s'évapore bien avant que la température de pyrolyse soit atteinte et même en autoclave; les pertes de produit sont trop importantes pour qu'une telle technique soit exploitable. Par contre, en utilisant un dérivé solide peu volatil de la borazine, par exemple un oligomère tel que le biborazinyne ou le borazanaphtalène, ou des mélanges de ces corps, cet inconvénient disparaît.

Pour préparer de tels dérivés de la borazine, on peut irradier celle-ci en phase vapeur au moyen d'une source actinique [M.A. Ness *et al.*, J.A.C.S. 94 (1972), 1438], ce qui provoque la formation de divers oligomères outre les dimères précités. On peut également polymériser la borazine par la chaleur (voir A. Laubengayer *et al.*). Tous ces corps sont utilisables dans la présente invention, pour autant qu'ils soient solubles en milieu organique volatil. On peut également utiliser des dérivés alcoylés de ces oligomères [voir G.A. Kline *et al.*, Inorg. Chem. 16 (1977), 11].

Le présent inventeur a, de plus, trouvé que les oligomères de la borazine sont préparables par irradiation de la borazine liquide, les radiations utiles se situant dans le visible et l'UV. Des traces de métaux de transition (Cr, Fe, Mo, W, etc.) peuvent catalyser une telle réaction.

Pour mettre en œuvre la présente invention, on procède de préférence comme suit: on prépare une solution du ou des composés boraziniques solides dans un solvant organique neutre, par exemple, benzène, toluène, dioxanne, THF, etc., et, dans cette solution, on trempe l'objet à revêtir. Cette technique présente l'avantage considérable de rendre accessibles au produit de revêtement tous les éléments de la surface de l'objet considéré, fussent-ils même difficilement atteignables par les réactifs gazeux dans le cas d'application des techniques de revêtement habituelles. Puis on retire l'objet de la solution et, après égouttage, on fait en sorte que le solvant s'évapore, ce qui laisse, à la surface de l'objet, une mince pellicule du dérivé borazinique solide. La concentration en dérivé borazinique de la solution peut être quelconque; plus elle est élevée, plus la pellicule obtenue par évaporation est épaisse. Pratiquement, des concentrations de 5 à 50% conviennent.

On chauffe ensuite l'objet dans un four sous atmosphère contrôlée, par exemple sous azote ou argon à une température suffisante pour provoquer la pyrolyse du dépôt et sa conversion en BN avec départ d'hydrogène. Cette température se situe de préférence dans la gamme des 600-800° C, ce qui fournit un dépôt amorphe, homogène et résistant à la corrosion par l'humidité et les agents chimiques corrosifs usuels (HF, acides minéraux et organiques, hydroxydes alcalins, NH_3 , etc.).

La couche borazinique étant très mince (de l'ordre de quelques μm à environ 500 μm), sa décomposition pyrolytique est très rapide et ne dure, en fait, que quelques secondes à quelques minutes (par exemple 10 s à 10 min). Elle s'applique donc aussi bien à un processus discontinu que continu au cours duquel l'objet (un ruban, un filament, ou une série d'objets disposés sur une bande transporteuse) est, successivement, trempé dans la solution, séché et chauffé par passage dans un four à la température considérée (le tout en atmosphère inerte).

Le dépôt obtenu vers 600-800 °C, amorphe, peut être cristallisé par chauffage à une température plus élevée; par exemple vers 1100-1300 °C, il se transforme en BN hexagonal qui, de par sa structure, présente des propriétés différentes de celles de la couche amorphe, mais également intéressantes industriellement.

Parmi les substrats métalliques et minéraux se prêtant à la mise en œuvre de la présente invention, on peut citer des articles comportant une surface d'un métal tel que Ti, Mo, Fe, Mn, Cr, Co, Ni et autres métaux usuels. Sur des métaux plus nobles tels que Cu, Ag, Au, Pt, Pd, etc., l'application du procédé est également possible, mais l'adhérence est moins satisfaisante. Comme substrats minéraux, on peut citer Al_2O_3 , SiO_2 , ZrO_2 , le verre, le grès, les céramiques, les métaux durs, les borures, carbures, nitrures métalliques, etc.

Les exemples qui suivent illustrent l'invention en détail.

Exemple 1:

Dans un récipient standard en quartz, on a placé, sous protection d'azote sec, 100 g de borazine liquide qu'on a soumise à irradiation par la lumière solaire. Après quelques jours, on a procédé à une distillation sous azote, ce qui a fourni 26 g de solide non distillable, la portion volatile étant constituée de borazine. Ce solide consiste en un mélange de borazanaphthalène, de biborazinyle et d'une faible quantité d'oligomères de poids moléculaire plus élevé, dont on n'a pas déterminé la structure.

On a obtenu des résultats similaires par irradiation de plus courte durée au moyen d'une lampe UV fournissant un flux de 20 W/cm à une distance de 30 cm. En présence de traces de composés de métaux de transition, le temps d'oligomérisation est encore raccourci.

Exemple 2:

Sous protection d'azote, on a dissous 25 g du solide tel qu'obtenu comme décrit ci-dessus dans 150 ml de benzène sec et, dans cette solution, on a immergé un faisceau d'environ 20 g de fibres d'alumine d'un diamètre de 20-40 μm . On a retiré cet écheveau de la solution et on l'a séché sous azote à 30-40 °C jusqu'à disparition complète du solvant.

On a alors rapidement chauffé à 800 °C, en atmosphère d'azote, ces fibres recouvertes d'une mince pellicule de composés boraziniques solides dans un four électrique. Après quelques minutes à cette température, on a retiré l'écheveau et, par analyse SEM, on a constaté la présence sur les fibres d'un film homogène de nitrure de bore amorphe. L'épaisseur de ce film était d'environ 0,5 μm . En répétant cet exemple avec des solutions de dérivé borazinique dont la concen-

tration variait entre 2 et 35% en poids, on a obtenu des films similaires dont l'épaisseur variait entre 0,1 et 2 μm . On a obtenu des résultats similaires sur d'autres substrats, par exemple des fibres ou fils de SiO_2 , Fe, Ni.

Par chauffage à 1250 °C, on a converti le revêtement amorphe d'une partie de ces fibres en nitrure de bore hexagonal adhérent, isolant et non poreux.

Exemple 3:

Sous protection d'azote, on dissout 25 g du solide borazinique tel qu'obtenu comme décrit à l'exemple 1 dans 150 ml de toluène sec et, dans cette solution, on immerge de façon continue une fibre optique de silice qui est ensuite séchée sous azote sec à 60-80 °C jusqu'à élimination complète du solvant. Par la suite on chauffe rapidement la surface de la fibre recouverte d'une mince pellicule de composés boraziniques solides entre 600 et 800 °C. On obtient ainsi un film protecteur de nitrure de bore amorphe d'une épaisseur de l'ordre de 0,4 micron. Cette couche assure une protection contre les agents chimiques et en particulier contre l'eau, compte tenu du caractère hydrophile de la couche. De plus, la couche assure également une protection mécanique et confère à la fibre un coefficient de friction peu élevé, ce qui est d'un grand intérêt pour la confection des câbles de transmission optique.

Exemple 4:

Sous protection d'azote, on dissout 20 g du solide tel qu'obtenu comme décrit à l'exemple 1 dans le trichloréthylène. Cette solution est pulvérisée au moyen d'un pistolet à la surface d'une plaque de verre (on pourrait aussi utiliser un métal ou une céramique) maintenue à 80 °C. Après disparition complète du solvant, il reste sur la surface du substrat une mince pellicule de composés boraziniques solides. On chauffe ensuite le substrat à des températures comprises entre 600 et 800 °C et on obtient ainsi une couche de nitrure de silicium amorphe.

Par chauffage à 1250 °C, on convertit le revêtement amorphe en nitrure de bore hexagonal adhérent, isolant et non poreux.

Exemple 5:

On procède comme dans l'exemple 4, mais, au lieu de chauffer tout le substrat à haute température, on dirige un faisceau laser sur une portion de celui-ci, de manière à ne chauffer que localement la fine pellicule de composés boraziniques solides qui le recouvre. On peut aussi utiliser un faisceau d'électrons ou d'ions. On obtient ainsi, localement, une couche de nitrure de bore hexagonale adhérente, isolante et non poreuse. En immergeant, sous atmosphère protectrice, le substrat dans le solvant utilisé pour dissoudre l'oligomère de borazine, on élimine la couche de composés boraziniques non transformés en BN par le faisceau laser. Avec cette technique, on dépose ainsi sur le substrat une couche de nitrure de bore hexagonale adhérente, isolante et non poreuse sous la forme d'une zone de dessin défini préalablement. Cette technique peut s'appliquer également à des substrats métalliques, vitreux, céramiques et autres. Cette technique offre, en conséquence, un grand intérêt dans le domaine de la fabrication de microcircuits électroniques.

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☒ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.